Finding Relevant Atomic Processes Using Accelerated Molecular Dynamics

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Study of thermally activated phenomena in solid-state materials at experimental laboratory length and time scales is essential for designing materials with desirable characteristics. In these materials, atomic processes that govern macroscopic phenomena often occur at time scales that are simply beyond the reach of atomistic simulation methods such as molecular dynamics (MD). As a result, current materials modeling techniques frequently make severe assumptions regarding the atomic processes in solid-state materials, assumptions that are likely to corrupt the dynamical evolution.

Over the last 10 years, a suite of accelerated molecular dynamics methods has been developed at LANL to overcome this challenge [1]. In particular, the temperature accelerated dynamics (TAD) method [2] is a powerful computational tool for studying thermally activated phenomena in solid-state materials over large time scales, such as seconds. In the TAD method, transitions from state to state are made to occur more rapidly by raising the temperature of the system. Although the wrong event sometimes occurs first at higher temperature, the TAD algorithm corrects for this, only allowing the correct events (with a desired confidence) to be accepted.

The TAD method gives statistically correct dynamics and it can reach large time scales. However, it is limited to small system sizes, e.g., 1000 atoms. We are pursuing different directions to develop multiscale methods for solid-state systems that overcome the materials length and time scale problem with the accuracy of the TAD method. One approach is to modify the TAD method so that it generates a proper list of reaction mechanisms as it proceeds. This list of processes and associated rate constants is then used in the well-known kinetic Monte Carlo (KMC) framework to advance the dynamics.

Based on this philosophy, we have developed a new formulation of the TAD method called the process list-TAD method (p-TAD). The method guarantees that all relevant processes at a particular temperature have been detected with a user-specified confidence over large time scales. This solves the long-standing problem of how to find a complete (or complete enough with desired confidence) list of KMC rate processes for a given system in a given state. Generation of such accurate KMC process lists, with error control, is not possible with any other currently available technique. Though the p-TAD algorithm resembles the original TAD algorithm in many ways, the p-TAD method introduces significant improvements to the existing TAD method. For example, it offers a more direct way to parallelize the dynamics for small (or large) systems, and it can be made more accurate event by event if desired, because the accurate rate constant is directly computed at low temperature. It also offers the possibility of including quantum dynamical (e.g., tunneling and zero-point) effects.

To test the capabilities of the p-TAD method we have studied the dynamics in silver deposited on a copper [Cu(110)] surface at several different silver coverages at a temperature of 150K. The simulations were performed using embedded atom potentials for silver and copper. A confidence measure of 95% was used for generating the list of processes. Figure 1 shows that long time scales (up to 0.1 s) were simulated with reasonably low CPU requirements by performing several high-temperature MD simulations that were each shorter than 1 ns. Several many-atom processes were repeatedly observed in the p-TAD calculations. Two examples of such processes are shown in Figs. 2 and 3. Typically, most many-atom processes are completely ignored in a conventional KMC method, which is a major drawback of the KMC method that can lead to incorrect model predictions in certain materials, such as irradiated and multicomponent materials. Unlike conventional KMC models, which often assume that atoms reside on a lattice (i.e., a fixed set of
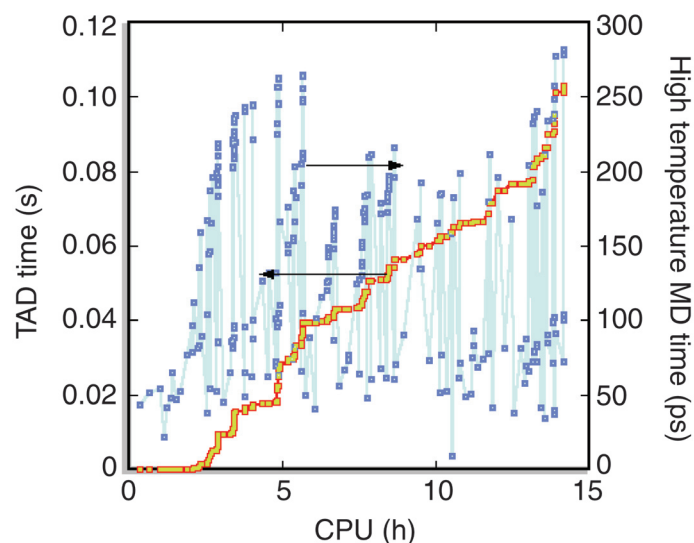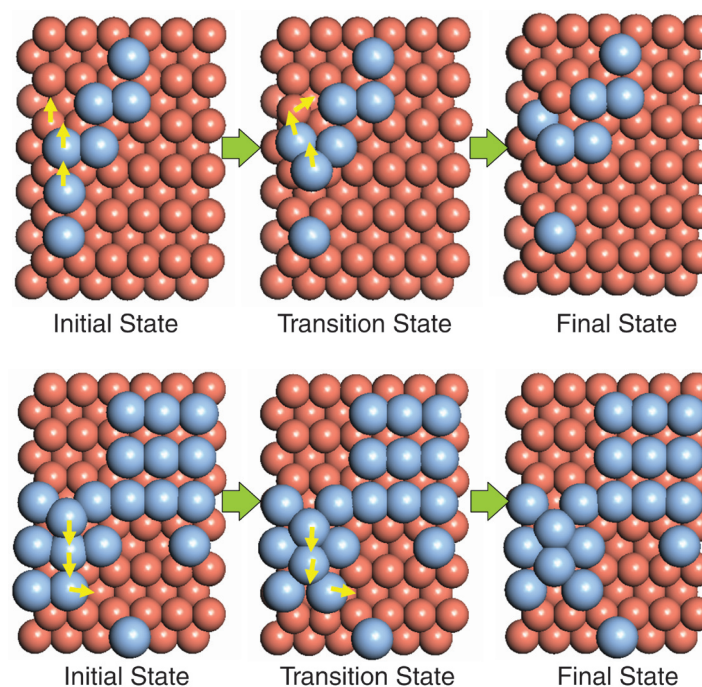
spatial positions), the TAD method does not have this restriction and it automatically allows for the strain relaxation resulting from the lattice mismatch between silver and copper atoms. This effect is visible in Figs. 2 and 3. Recently, the adaptive KMC method [3] has been developed by Henkelman and coworkers in an attempt to perform off-lattice KMC calculations by building a reasonably complete process list [4] via random transition state searches for a given state of the system. We believe that the TAD method, which follows the actual dynamics, offers a more correct way of establishing that *all* relevant KMC processes for a particular duration of time have been found with a certain confidence in a consistent manner.

In conclusion, we have demonstrated the strengths of a new variation of the TAD method called the p-TAD method. The p-TAD method is currently being further developed into the TAD-based KMC method. The latter builds on the former by generating process lists for small subsets of atoms. It combines the best of molecular dynamics, accelerated molecular dynamics, and kinetic Monte Carlo methods, to reach greater time scales, length scales, and accuracy

than has been possible previously. The resulting computer program will be used to study materials under irradiation and other problems.

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Initial State   Transition State   Final State

Initial State   Transition State   Final State

Fig. 1. Accelerated time accessed during a 14-hour p-TAD simulation of silver deposited on copper. The high temperature molecular dynamics time is also plotted.

Fig. 2. Initial, transition, and final states for a three-atom process involving silver (blue) and copper (brown) atoms at 0.19 ML silver coverage. The activation barrier for this process is 0.74 eV.

Fig. 3. Initial, transition, and final states for a three-atom process involving only silver (blue) atoms at 0.53 ML silver coverage. The activation barrier for this process is 0.35 eV.